

Scholars Research Library

Archives of Physics Research, 2014, 5 (6):19-28 (http://scholarsresearchlibrary.com/archive.html)



Crystal Growth and Physical Properties of KDP Admixtured TGS Single Crystals

A Abu El-Fadl^{*} and A. M. Nashaat

Physics Department, Faculty of Science, Assiut University, 71516 Assiut, Egypt

ABSTRACT

Potassium dihydrogen phosphate (KDP)Admixturedtriglycinesulphate (TGS) single crystal (KDPTGS) with concentration of KDP in the growth solutions varied from 10mole% to50mole% has been grown by the slow evaporation technique. Crystal structure was studied by x-ray powder diffraction. KDPTGS crystallizes in the monoclinc system with $P2_1/c$ space group.X-ray analysis showed a slight variation in the lattice parameters for admixtured crystals. The absorption spectra for pure and KDP doped TGS crystals have significantly low cut-off wavelengths and good transmittances towards the visible and infrared regions. By increasing KDP concentration, the optical transmittance increases, however the cut-off shifts to lower wavelengths. The optical data are analyzed and interpreted in terms of allowed indirect transitions. The optical energy gap (E_g) has the value of 4.912eVfor pure TGS crystal. This value increases with increasing KDP concentration and tends to saturate ata doping concentration of 30mole% KDP. The modes of vibration of different functional groups present in the grown crystals were identified by the FTIR spectral analysis.

Keywords: KDPTGS crystals, Growth from solutions, X-ray diffraction, Optical band gap, FTIR spectra.

INTRODUCTION

Recently, there is an increasing interest in triglycinesulphate $[(NH_2CH_2COOH)_3H_2SO_4](TGS)$ crystals since it may have useful properties for various optoelectronic applications in the visible and infrared spectral ranges. TGS crystal has good pyroelectric properties. It exhibits strong absorbing ability in the most part of infrared region. At room temperature, its pyroelectric coefficient value is the highest. It is a material of choice for high speed broad band infrared pyroelectric detectors and vidicon [1-3].

Ferroelectric properties of TGS crystals have been found to change under the influence of different kind of doping [4,5]. Previous work on the modification of the ferroelectric properties of TGS by the addition of dopants such as inorganic ions [6,7] as well as with partial substitution of L-alanine have been investigated [8]. The importance of TGS crystals doped with organic molecules arised from the observation that the infrared detection parameters increased after doping TGS with some organic molecules. The increase in the detection parameters improves the sensitivity of the IR detectors constructed using these crystals [9-12].

C.S. Fang et al. [13] have grown TGS crystals, with Mn⁺² and Li⁺as dopants. It was found that the addition of dopants increases the pyroelectric coefficients of TGS crystals. Abu El-Fadl[7]studied the effect of divalent-ions-doping on the absorption spectra and optical parameters of triglycinesulphate crystals. Doping TGS crystals with small concentrations of divalent ions considerably affects the measured optical parameters. The effect, however, varies from one dopant to another according to their physicochemical activity. Batraet al. [14] have investigated the influence of rare earth metal ions on dielectric, pyroelectric and piezoelectric properties of TGS crystals. It is observed that samarium, ytterbium and terbium doped TGS crystals possesses low dielectric constant, pyroelectric coefficients and high Vickers's hardness.

The study of the physical properties of TGS mixed with ferroelectric and antiferroelectric crystals have received much less attention. Potassium dihydrogen phosphate family crystals (KDP, DKDP,ADP) are among the materials most widely used in nonlinear optics, optoelectronics and photonics. Such crystals possess a unique set of properties, including wide transparency range, high laser damage threshold, and can be grown large sized. This gives rise to their reasonable application as large aperture frequency converters of laser radiation and electro-optic switches in powerful laser systems for inertial confinement experiments[15,16]. KDP-doped TGS (TGSK) crystals, which had doping concentrations of 10, 25, 35, 40, and 45mole% were grown from saturated solutions by Sooman Lee et al. [17]. They investigated the influence of the KDP doping on the pyroelectric and the dielectric properties of the TGS crystal. With increasing KDP doping, the coercive field increased. Moreover, improved pyroelectric properties were observed for the grown crystal containing 25 mole% KDP to H_2SO_4 . Thus, the optimum doping of KDP in the TGSK crystal allows them to obtain a high value of the pyroelectric TGS crystals. It is found that incorporated dopant revealed in shift of Curie point to lower temperature with increase in dopant concentration. Micro hardness studies have shown that the hardness decreases with increase in ADP concentration.

In the present investigation results on crystal growth, structural and optical absorption spectra and optical parameters of TGS crystals incorporated with different concentrations of KDP crystal has been carried out on the search for the suitable dopant which gives TGS the desired properties relevant for applications.

MATERIALS AND METHODS

2- Experimental

2.1. Synthesis and crystal growth

Pure TGS and KDP doped TGS crystals were grown by solution growth method. A solution of KDPTGScompound was synthesized by dissolving KDP in TGS in the ratio10, 20, 30, 40 and 50mole% relative to H_2SO_4 in double distilled water according to the equation:

$$x(KH_2PO_4) + 3(NH_2CH_2COOH) + (1-x) H_2SO_4 \rightarrow KDPTGS$$
(1)

The solution was left for evaporation to seeding at room temperature (298 K). A good seed was chosen, and then it was employed for the growth of single crystal.

Single crystal of KDPTGS was grown by the slow evaporation technique of an aqueous solution at constant temperature (315 K) by using an indigenous crystal growth apparatus fabricated in the laboratory. Optically good quality seed crystals were suspended firmly inside the solutions using a nylon thread. The regime of the crystallization was made identical for all the crystals. After 3~4 weeks, crystals with the dimensions of $5x2x2 \text{ cm}^3$ could be harvested and transparent, flawless crystals of optical quality and with well-developed faces were obtained. As shown in the photograph ofFig.1, the grown single crystal was colorless and optically transparent. Doping of KDP in TGS solution results in the modification of the crystal morphology. The relative growth velocity normal to the growth axis is altered and hence the doped crystal morphology is different from the pure system. It has been found by the elemental analysis that the dopant concentration in the solution (x_s) is far higher than the concentration in the crystal (x_c) for TGS crystals grown with different concentrations of KDP. It was reported by Nakatani et al.[19]for phosphoric acid doped TGS crystals, that the ratio of x_c/x_s at the maximum is 10^{-2} .

2.2. Characterizations

2.2.1. Powder x-ray diffraction measurements

For powder x-ray diffraction measurements, a sample was taken from the crystal and it was grated very well until it became soft powder. Then, small amount from this powder was taken to use in these measurements. The measurements were performed at room temperature using a Philips (PW1710) diffractometer, which is equipped with a curved graphite crystal monochromator, an automatic divergence slit, a vertical goniometer (PW1050) with automatic sample changer and Xenon proportional detector. The measurements were swapped from $2\theta=4^{\circ}$ to $2\theta=80^{\circ}$ with step of 0.04°, copper target with nickel filter at 40 kV, 30 mA, a scanning speed of 0.06°/min and incident wavelength was 1.5418 Å.

2.2.2. FTIR spectra

The FTIR spectra were recorded in the range 400-4000 cm⁻¹ employing a NICOLET FTIR 6700 spectrometer by the KBr pellet method to study the functional groups of the samples.

2.2.3. Optical transmission

Cleaved rectangular b-cut plates about 20 mm² in area and 1 mm in thickness specimens were prepared and then polished on a wet piece of soft cloth to be used for optical measurements. The prepared plates were clear and free from noticeable defects. Specimens prepared with these dimensions to fit the sample holder, and the sample was fixed to the holder by special glue. The optical transmission spectra measured in the photon energy range 190-900 nm at room temperatures were determined using Shimadzu UV-VIS-2101 PC dual beam scanning spectrophotometer. The samples used for optical measurements were clear, transparent and free from any noticeable defects. The incident unpolarized light was nearly perpendicular to b- plane. The surrounding medium was air.

RESULTS AND DISCUSSION

3.1. X-ray diffraction

The powder XRD patterns of KDP admixtured TGS crystals compared with that of pure TGS are depicted in Fig.2. The results of the XRD patterns indicate that the peak positions of the grown crystals were located in approximately the same positions as that of pure TGS and slightly shifted in doped crystals, but the intensities of the diffracted peaks are found to be varied. The sharp peaks confirm that the crystallinity of the grown crystals is good. The crystalline perfection of the specimen crystals is extremely good without having any internal structural grain boundaries and mosaic nature.

It is clear from the diffractograms that, there are no extra peaks other than the sharp indexed ones, the mixtures of TGS and KDP are of single phase belonging to monoclinic lattice structure with the space group P2₁/c, according to ICDD (PDF file 14-0873). Small change in the lattice constants in the doped crystals can be attributed to the packing consideration arising from the individual K^+ and S^+ ions with different ionic radii. The unit cell parameters and the cell volume of the pure and doped TGS crystals are presented in Table1. The lattice parameters of pure TGS are in agreement with the reported values by Theresita et al.[20]. In the case of doped TGS crystals, slight variations in the values of lattice parameters and cell volume are observed. It implies that KDP doping have been incorporated to the lattice of TGS crystals. Because of doping there may be some defects or strains in grown crystals. Similar observations on phosphate added TGS crystals have been reported by others[21]. The lattice parameters of pure and phosphate doped crystals show a significant difference in spite of the low incorporation of H₃PO₄ while the monoclinic angle βincreased [21].

Farhana Khanum et al. [22] have grown TGS crystals with nickel sulphate as dopant. It is found that the lattice parameters are slightly distorted due to the incorporation of nickel ion into the lattice sites of the TGS crystal. Single crystals of ADP-doped TGS were grown from aqueous TGS solution containing 20 mole% of ADP by Arunmozhi et al. [23]. They concluded that the antiferroelectric properties of ADP do not have an influence on the ferroelectric properties of TGS and ADP acts more like an impurity or dopant. No internal bias field is created and hence nonpolar effects are generated with ADP doping. Increase in the coercive field values in ADPTGS shows that the dopant restricts dipoles from switching.

KDP ratio (mole%)	a (Å)	b (Å)	c (Å)	β (deg.)	Vol. (Å) ³
0 (pure)	9.1676	12.6545	5.7293	105.5	640.5
10	9.1656	12.6517	5.731	105.5	640.4
20	9.1666	12.6554	5.7296	105.53	640.4
30	9.1695	12.6517	5.7323	105.53	640.7
40	9.1671	12.6522	5.7349	105.57	640.8
50	9.174	12.6586	5.7305	105.53	641.2

Table 1 Powder XRD data of KDPTGS crystals.

3.2. FTIR spectra

On the basis of the available data, recorded FTIR spectrum of different functional groups of KDPTGS crystals is shown in Fig.3. The observed wave numbers, relative intensities obtained from the recorded spectra and the assignments reported for grown crystals are cited in Table2.

The stretching of N–H mode of NH₃ group and O–H of hydrogen bonded carboxyl groups appears at the range 3114-3207 cm⁻¹. The peaks appears at the range 1704-1714 cm⁻¹ and 906-911 cm⁻¹ are assigned to the C=O symmetric stretching and C–C stretching. The peaks at the range 1616-1624 cm⁻¹ are assigned to asymmetric stretching of COO and bending of NH₃ group. The characteristic peaks observed in the range 1394-1436cm⁻¹ are assigned for C–O–H bending vibration and CH₂ bending. The peaks at the range 1308-1311 cm⁻¹ are assigned to the S=O asymmetric stretching and CH₂ twisting. C–O stretching vibration and CH₂ rocking occurs at range 1124-1142 cm⁻¹. The torsional oscillation of NH₃ group and C–N bending occurs at the range 613-647 cm⁻¹. The peaks appear at the range

558-572 cm⁻¹ are assigned to SO₄ symmetric stretching. The peaks at the range 495-506 cm⁻¹ are assigned to torsional vibration of C–N and NH₃.

KDP doped samples provide very similar features as those of pure TGS. More bands were located at the same positions as those of pure TGS. There is a very slight shift observed in band positions compared to pure one. But doped samples provide less resolution of bands. Some bands are broadened and some are narrowed. Degeneracy is more for doped samples than that of pure TGS. Our results match well with the values reported by Kartheeswari and Viswanathan.[24] and Parimaladevi et al. [25]. On the other hand, optical quality single crystals of pure and ADP admixture TGS were grown and their FTIR spectra confirm the presence of the dopant qualitatively. Also the antiferroelectric properties of ADP have no influence on the ferroelectric properties of TGS and ADP acts more or like an impurity or dopant. Shift in T_c shows that inhomogeneous dopant incorporation leads to micro regions during crystal growth with different transition temperatures[18].

TGS pure	10% KDP	20% KDP	30% KDP	40% KDP	50% KDP	Range	Assignment	
3203	3205	3152	3207	3120	3166	3114- 3207	Symmetric stretching (N-H mode) of NH ₃ group and O-H stretching of hydrogen bonded carboxyl groups	
1705	1708	1706	1708	1709	1715	1704- 1714	Symmetric stretching (C=O)	
1623	1619	1616	1621	1625	1619	1616- 1624	Asymmetric stretching (COO) and bending of NH_3 group	
1426	1426	1426	1427	1395	1436	1394- 1436	(C-O-H) bending vibration and CH ₂ bending	
1309	1309	1309	1309	1311	1310	1308- 1311	S=O asymmetric stretching and (C-C) symmetric stretching and CH ₂ twisting	
1126	1127	1143	1134	1129	1125	1124- 1142	CH_2 rocking and SO_4 symmetric stretching and it can be assigned to C-O stretching	
908	907	911	907	907	903	903-911	(C-C) stretching	
646	646	646	646	647	647	(12 (17	Transianal assillation of NUL answer and (C.N.) handing	
623	615	623	615	613	618	- 013-047	rorsional oscillation of Nri3 group and (C-N) bending	
572	573	582	571	571	571	558-572	Symmetric stretching of SO ₄	
500	500	496	502	499	507	495-506	Torsional vibration of (C-N) and group NH ₃ oscillations	

Table2 The observed IR frequencies and corresponding assignments.

3.3. UV-VIS spectral analysis

The behavior of the spectral dependence of the optical transmittance (T) as functions of both the KDP concentration (from 10 to 50mole%) and wavelength (from 230 to 270 nm) are presented in Fig.4. In general, the transmittance increases with increasing KDP concentration. From the UV spectrum, KDPTGS crystals are found to be transparent in the UV region. The inset of Fig.4, shows the transmittance of pure TGS sample in the range of wavelengths (from 200 to 900 nm). It can be seen from the transmission spectrum and Fig. 5, that the lower cut-off wavelength lies nearly at 240 nm for pure TGS crystal. Thus lower cut-off value decreases due to KDP doping. The absorption is negligible in the entire visible region of the electromagnetic spectrum. The transmission extends nearly from 240 nm to 1100 nm, makes it suitable for the applications for NLO materials having nonlinear optical applications.

Good optical transmittance and lower cut-off wavelengths are very important properties for lasers, holographic recording, optical filters, and nonlinear optical applications. It was observed by Khanum et al [4],that pure and potassium bromide doped TGS crystals exhibit high transmission in the entire visible region. TGS crystal, doped with 1mole% KDP was grown by Deepti and Shanti [26]. Their UV-VIS spectra show that the grown crystal was optically transparent through 200-800 nm and hence suggests the suitability of this material for optical devices. The effect of Thiouea-doped triglycinesulphate (TuTGS) on machining the crystal for device purposewas studied by Krishnakumar et al. [27]. It was found that, the doped crystal exhibit excellent transmission in entire UV-VIS range studied than undoped crystal. This property enables the material for the fabrication of IR detectors and in some optoelectronics device technology. Also sufficient shift in the lower cut-off wavelength towards UV region in doped crystal makes this material to find application in generation of UV light. Another study by Farhana Khanum and JibanPodder [22] of pure and NiSO₄ doped TGS crystals, showed, that the transmission percentage of NiSO₄ doped TGS is lower than pure TGS and the transmission decreases with increase in dopant concentrations.

The percentage of optical transmission and the UV transparency cut-off limits data are tabulated in Table 3. The UV transparency cut-off limits decreases with the doping concentration. Similar results have been obtained in the case of L-alanine doped KDP [28] and also lithium doped L-alanine crystals [29]. From the spectra and Table3, it is found that the cut-off wavelength for the pure and doped crystals was found to be increased with doping concentration up to 20 mole% and above this it decreases. The cut-off wavelengths are around 230-240 nm and the maximum

transmission levels are in the wavelength range 250-800 nm which are most desirable characteristic of a NLO material for applications. As there is no absorption in the visible region, these crystals are suitable for NLO applications. The cut-off wavelengths and the transmission levels are in good agreement with the reported values by RezagholipourDizaji and Naseri [21]. It is observed from their spectrum, that the transmittance percentage of the TGSP crystal is higher than that of the TGS crystal. The lower cut-off wavelength is around 226 nm for TGS crystal grown by unidirectional method. The same cut-off wavelength was reported by Pandian et al. [30] for pure TGS crystal grown by the S-R method.

The absorption spectra of KDPTGS single crystals have been investigated at photon energies near the fundamental absorption region, and the optical absorption coefficient (α) was calculated using the relation:

 $\alpha = 2.3026 \log (1/T) / t$ (2)

Where *T* is the transmittance and *t* is thickness of the crystal.

The results of the absorption coefficient α against photon energy hv for pure TGS crystal as well as for crystals doped with different KDP concentrations are plotted in Fig. 6. The general feature of the figure is the continuous increasing of α with increasing photon energy. At the absorption edge α increases rapidly with hv. As it is clear, doping decreased the absorption coefficient of KDPTGS at all energies and concentrations.

The predominate mechanism, band-to-band transitions was determined by the analysis of the α =f(v) dependence. In the high-absorption edge, the photon energy dependence of the absorption coefficient can be described by the parabolic relation [31];

 $\alpha h \nu = A (h \nu - E_g)^s \qquad (3)$

where v is the frequency of the incident photon, h is Planck's constant, A is a constant, E_g is the optical energy gap and s is the number which characterizes the optical processes, and s has the value ½ for the direct allowed transition, and 2 for the indirect allowed transition. When the straight portion of the graph of $(\alpha hv)^{1/s}$ against hv is extrapolated to α =0 the intercept gives the transition hand gap. The experimental results for the investigated TGS crystals at different KDP dopant concentration show a good fit to Eq. (3) with s =½ indicating that the indirect photon transitions is the most probable mechanism. The optical band gap E_g , of the indirect transition can be obtained, and the following equation can then be applied to this sort of interband transition:

$$(\alpha h\nu)^{1/2} = A(h\nu - E_g)$$
(4)

The optical band gap E_g of the indirect transition can be obtained from the intercept of the $(\alpha hv)^{1/2}$ vs. hv plots with the energy axis at $(\alpha hv)^{1/2} = 0$, as, shown in Fig.6. The values of the indirect optical energy gap as a function of KDP concentration are plotted in Fig.7. It is evident upon inspection of Fig.7.that the increase of KDP concentration leads to an increase of the band gap E_g and saturates at 30 mole% of KDP doping. Same data are presented by Parimala devi et al. [25]. Their single crystal and powder XRD studies confirmed that a certain amount of HNO₃ is doped into TGS and that there is saturation in the doping level already at 20 mole% HNO₃ addition. Further increase in HNO₃ content in solution acted as additive and enabled the changes only in crystal habit.

KDP concentration (mole%)	Cut-off wavelength (nm)	Optical energy gap (eV)
0(pure)	239.0	4.912
10	239.5	4.915
20	240.5	4.928
30	238.5	4.963
40	238.0	4.966
50	237.0	4.969

Table3 Cut-off wavelength and optical energy gap for KDP doped TGS crystals.

In general, one can observe that the optical energy gap increases with increasing the KDP concentration (the results are summarized in Table3). This increase of energy gap with KDP incorporation can be attributed to the variation of disorder and defects presented by doping.



Fig. 1. Photograph of as grown KDPTGS single crystals.



Fig. 2. Powder XRD patterns of KDPTGS crystals.



Fig. 4. UV-Visible-NIR transmittance spectrum (inset) pure TGS spectrum in the whole measured range of wavelengths.

Scholars Research Library



Fig. 5.The cut-off wavelength against KDP Concentration of KDPTGS single crystals.



Fig. 6. Absorption coefficient (α) for KDPTGS crystals

Scholars Research Library



Fig. 7. Plot of (ahv)1/2 verses photon energy of KDPTGS crystals.



Fig. 8.Optical energy gap (E_g)against KDP concentrationof KDPTGS crystals.

CONCLUSION

Single crystals of potassium dihydrogen phosphate doped triglycinesulphate(KDPTGS) were grown from slow evaporation solution growth technique. Powder x-ray diffraction analysis was used to estimate the cell parameters and the compound easily crystallizes in monoclinic system with space group $P_{1/c}$. and the powder x-ray diffraction pattern of the grown crystals was indexed. The UV visible spectral shows that the grown crystals have optical transparency. By using the transmittance spectrum, the absorption edge was calculated, and the type of transition is the allowed indirect one. Significant changes in the activation energies of doped crystals were identified. Improvement in the transparency of the TGS crystal on the addition of KDP highlights their prospects as a candidate for optoelectronic applications in visible and infrared region. The modes of vibration of different molecular groups present in the sample were identified by the FTIR spectral analysis.

REFERENCES

[1] J. Logeswario, Optoelectronics and advanced materials, 2008, 2,630.

[2] NidhiSinha, NeetiGoel, B.K. Singh, M.K. Gupta, Binay Kumar, J. Sol. State. Chem., 2012, 190, 180.

[3] H.V. Alexandru, C. Berbecaru, F. Stanculescu, L. Pintilie, I. Matei and M. Lisca, Sens. Actuators A, 2004,113, 387.

[4] FarhanaKhanum, JibanPodder, Crystallization Process and Technology, 2011, 1,26.

[5] G. Ravi, S. Anbukumar, P. Ramasamy, Mater. Chem. Phys., 1994,37,180.

[6] A. Abu El-Fadl, *Physica B*,1999,269,60.

[7] A Abu El-Fadl, J. Phys. Chem. Solids, 1999, 60, 1881.

[8] Dagmar Barosova, Stanislav Panos, Sens. Actuators A,2004, 110, 350.

[9] C.M. Raghavan, R. Sankar, R. Mohan Kumar, R. Jayavel, *Mater. Res. Bull.*,2008, 43,305.

[10] S. Genbo, H. Youping, Y. Hongshi, S. Zikong, W.Qingjin, J. Cryst. Growth, 2000, 209, 220.

[11] A. T. Ravichandran, A. Judith Jayarani, International Journal of Science and Research (IJSR) 2014,3, 2323.

[12] M. A. Gaffar, G. F. Al-Noaimi, and A. Abu El-Fadl, J. Phys. Soc. Jpn., 1989,58,3392.

[13] C.S. Fang, Yao Xi, A.S. Bhalla, L.E. Cross, Mater. Res. Bull., 1983, 18, 1095.

[14] A.K. Batra, PadmajaGuggilla, Dewanna Cunningham, M.D. Aggarwal, R.B. Lal, Physica B, 2006, 371, 210.

[15] C. Maunier, P. Bouchut, S. Bouillet, H. Cabane, R. Courchinoux, P. Defossez, et al., Opt. Mater., 2007, 30, 88.

[16] I.M. Pritula, A.V. Kosinova, O.N. Bezkrovnaya, M.I. Kolybaeva, V.M. Puzikov, A.V. Lopin, et al., *Opt. Mater.*, **2013**, 35, 2429.

[17] Sooman Lee, Kyewan Lee, Gwangseo Park, Journal of the Korean Physical Society, 1997, 30, 261.

[18] T. Balu, T.R. Rajasekaran, P. Murugakoothan, J. Current Appl. Phys., 2009, 9, 435.

[19] Noriyuki Nakatani, Masakazu Yoshio, Jpn. J. Appl. Phys., 1996,35, 5752.

[20] N. TheresitaShanthi, P. Selvarajan, C. K. Mahadevan, Indian Journal of Science and Technology, 2009, 2, 49.

[21] H. RezagholipourDizaji, Z. Naseri, Chinese journal of physics, 2013,51, 766.

[22] FarhanaKhanum, JibanPodder, Journal of Crystallization Process and Technology, 2011, 1, 49.

[23] G. Arunmozhi, S. Lanceros-Méndez, E. de Matos Gomes, Mater. Lett., 2002,54, 329.

[24] N. Kartheeswari, K. Viswanathan, Journal of Spectroscopy, 2013,2013,1.

[25] R. Parimaladevi, C. Sekar, V. Krishnakumar, Spectrochim. Acta, Part A, 2010,75,617.

[26] P. R. Deepti, J. Shanti, J. Sci. Res., 2014,6, 1.

[27] V. Krishnakumar, S. Sivakumar, R. Nagalakshmi, S. Bhuvaneswari, M. Rajaboopathi, Spectrochim. Acta, Part A,2008,71,480.

[28] K. D. Parikh, D. J. Dave, B. B. Parekh, M. J. Joshi, Cryst. Res. Technol., 2010, 45, 603.

[29] B. Suresh Kumar, M. R. Sudarsana Kumar, K. BajendraBabu, Cryst. Res. Technol., 2008, 43, 745.

[30] M. SenthilPandian, P. Ramasamy, Binay Kumar, Mater. Res. Bull., 2012,47,1587.

[31] A.K. Abbass, F.Y.M. Al-Eithan, J. Phys. Chem. Solids, 1986, 47, 933.